International Standard

ISO 21068-1

Second edition
2024-05

Chemical analysis of raw materials and refractory products containing silicon-carbide, silicon-nitride, silicon-oxynitride and sialon —

Part 1: General information, terminology and sample preparation

Analyse chimique des matières premières et des produits réfractaires contenant du carbure de silicium, nitrure de silicium, oxynitrure de silicium et sialon —

Partie 1: Informations générales, terminologie et préparation des échantillons

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Contents

Page

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Foreword

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This document was prepared by Technical Committee ISO/TC 33, *Refractories,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 187, *Refractory products and materials,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 21068-1:2008), which has been editorially and technically revised.

The main changes are as follows:

— The Scope was adjusted according to the Scope of the revised versions of ISO 21068-2, ISO 21068-3 and ISO 21068-4;

— Table 1 was removed as this is now part of the revised versions of ISO 21068-2, ISO 21068-3 and ISO 21068-4;

— The list of documents in Clause 2 has been adjusted;

— Clause 3 was adjusted to the revised versions of ISO 21068-2, ISO 21068-3 and ISO 21068-4;

— The weighing procedure has been removed as it can be assumed as general knowledge of the user of the ISO 21068 series;

— Bibliography was adjusted to this document.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Introduction

The ISO 21068 series has been developed from the combination of EN 12698-1:2007[1] and EN 12698-2:2007[2] and ISO 21068-1:2008[3], ISO 21068-2:2008[4] and ISO 21068-3:2008[5]. The last three standards have been originally developed from the combination of Japanese standard JIS R 2011:2007[6] and work items developed within CEN. Because there is a wide variety of laboratory equipment in use, the most commonly used methods are described.

ISO 21068-4 is derived from EN 12698-2:2007[2] describing XRD methods for the determination of mineralogical phases typically apparent in nitride and oxynitride bonded silicon carbide refractory products using a Bragg-Brentano diffractometer.

The ISO 21068 series is applicable to the analysis of all refractory products as classified in ISO 10081-1[7], ISO 10081-2[8], ISO 10081-3[9] and ISO 10081-4[10] (shaped) and ISO 1927-1[11] (unshaped) and raw materials containing carbon and/or silicon carbide. Therefore, the ISO 21068 series covers the full range of analysis from pure silicon carbide to oxide refractory composition with low-content silicon carbide and/or nitrides. Primarily, the ISO 21068 series provides methods to distinguish between different carbon bound types like total carbon (C_{total}) and free carbon (C_{free}) and derives from these two the silicon carbide content. ISO 21068-4 includes details of sample preparation and general principles for qualitative and quantitative analysis of mineralogical phase composition. Quantitative determination of α-Si_3N_4, β-Si_3N_4, Si_2ON_2, AlN, and SiAlON are described.

If free carbon is present, ISO 21068-2 includes different temperature treatments to determine the mass changes gravimetrically. Frequently, the resulting residue is used for other determinations.

The determination of other groups of analytes described in the ISO 21068 series are free metals, free silicon (Si_{free}), free aluminium (Al_{free}), free magnesium (Mg_{free}), free iron (Fe_{free}) and the group of oxides from main to trace components.

The ISO 21068 series also describes the determination of silicon dioxide, total silicon, oxygen and nitrogen and other oxide bound metals that typically occur in the materials.

It represents a listing of analytical methods which is generally structured according to material composition. However, it is still the user who should prove the applicability of the method depending on the material and analytical requirements.

The most broadly used analytical techniques such as X-ray fluorescence spectroscopy (XRF) and inductively coupled plasma-optical emission spectrometry (ICP-OES) suffer from the disadvantage that the analytical results are chemical species independent. For carbon-containing ceramic raw materials and compositions, the ISO 21068 series provides analytical methods for the determination of free carbon, and SiC in the presence of oxide compounds in particular SiO_2.

Due to the diversity of laboratory equipment, the ISO 21068 series summarizes broadly used analytical techniques which lead to equivalent results. For example, the determination of carbon is based on all described methods on the reaction of carbon with oxygen at elevated temperatures to CO_2. Thus, carbon is analysed as CO_2.

As well as carbon and carbide compounds, metallic silicon, aluminium and magnesium are considered. While metallic silicon is mainly a precursor material which remains after the production process of SiC in the raw material, metallic aluminium is added as an antioxidant in carbon-containing refractory formulations.

Mostly oxide bound components, such as Al_2O_3, CaO, MgO, TiO_2, Cr_2O_3, ZrO_2 and alkalis, can be determined by XRF, ICP-OES or wet chemical methods (see ISO 12677, ISO 26845[12], ISO 21587-1[13], ISO 21598-2[14] and ISO 21587-3[15]). These results can be corrected by formulae provided by the ISO 21068 series, in consideration of the values obtained by the determination of carbon, SiC, and metallic components.

The ISO 21068 series also provides methods for qualitative and quantitative determinations of the nitrogen content and the determination of oxygen. Thereby only the total content of nitrogen and oxygen is given; a precise determination of non-carbide components (oxides and nitrides) is not possible in this way.

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The ISO 21068 series also provides methods to distinguish quantitatively between different varieties of nitrides like silicon nitride, silicon oxy-nitride and sialon.

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Chemical analysis of raw materials and refractory products containing silicon-carbide, silicon-nitride, silicon-oxynitride and sialon —

Part 1: General information, terminology and sample preparation

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1 Scope

This document gives definitions and specifies techniques for the preparation of samples for the chemical analysis of silicon-carbide-containing raw materials and refractory products including:

a) SiC raw materials;

b) graphite brick containing silicon carbide;

c) silicon carbide brick (includes the bricks containing silicon nitride, silicon oxynitride, sialon);

d) refractories containing carbon and/or silicon carbide mixed with clay;

e) refractories containing carbon and/or silicon carbide mixed with silica (and fused silica);

f) refractories containing carbon and/or silicon carbide mixed with high alumina material;

g) refractories containing carbon and/or silicon carbide mixed with magnesia (and dolomite);

h) refractories containing carbon and/or silicon carbide mixed with chrome mineral or magnesia-chrome materials;

i) refractories containing carbon and/or silicon carbide except those described in a) to h) above.

The items of analysis described in ISO 21068-2, ISO 21068-3 and ISO 21068-4 are as follows:

— loss on drying (LOD);

— loss on ignition (LOI);

— total carbon, C_{total};

— free carbon, C_{free};

— silicon carbide, SiC;

— free silicon (Si_{free});

— free aluminium (Al_{free});

— free magnesium (Mg_{free});

— free iron (Fe_{free});

— silicon(IV) dioxide (SiO_2);

— aluminium(III) oxide (Al_2O_3);

— iron(III) oxide (Fe_2O_3);

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— titanium(IV) oxide (TiO_2);

— calcium oxide (CaO);

— magnesium oxide (MgO);

— sodium oxide (Na_2O);

— potassium oxide (K_2O);

— chromium(III) oxide (Cr_2O_3);

— zirconium(IV) oxide (ZrO_2);

— boron oxide (total boron calculated as B_2O_3);

— nitrogen;

— oxygen;

— nitrides (undifferentiated: Si_3N_4, AlN, BN, sialon, oxy-nitrides, etc.);

— mineralogical phases (XRD-methods).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5022, *Shaped refractory products — Sampling and acceptance testing*

ISO 8656-1, *Refractory products — Sampling of raw materials and unshaped products — Part 1: Sampling scheme*

ISO 12677:2011, *Chemical analysis of refractory products by X-ray fluorescence (XRF) — Fused cast-bead method*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
monolithic (unshaped) refractory material
mixture consisting of an aggregate and a bond or bonds, prepared ready for use either directly in the condition in which they are supplied or after the addition of one or more suitable liquids

Note 1 to entry: They can contain metallic, organic or ceramic fibre material.

Note 2 to entry: These mixtures are either dense or insulating. Insulating mixtures are those whose true porosity is not less than 45 % (*V*/*V*) when determined in accordance with ISO 5016[16] using a test piece fired to specified conditions.

Note 3 to entry: Monolithic (unshaped) materials are classified in ISO 1927-1[11].

[SOURCE: ISO 1927-1:2012[11], 3.1, modified — "(*V*/*V*)" has been added to Note 2, Note 3 to entry has been added.]

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3.2
dense shaped refractory material
pre-shaped and fired or tempered refractory compositions to obtain a ceramic or a carbon-based bonded product having a true porosity of less than 45 % (V/V)

[SOURCE: ISO 5017:2013[17], 3.10, modified — the part "pre-shaped……bonded" has been added.]

Note 1 to entry: Dense shaped refractory materials are classified in accordance with ISO 10081-1[7], ISO 10081-2[8] ISO10081-3[9] and ISO 10081-4[10].

3.3
moisture
water which is not chemically bound in refractory raw materials and products, derived from moisture absorption during manufacture, storage, or residual water used for the preparation of a refractory castable mix

3.4
volatile component
component which is evolved at 250 °C in air and at 750 °C in argon atmosphere

Note 1 to entry: In general, attached and chemically bound water, hydroxyl groups as well as all volatile compounds from pitch- or resin-bonded formulations are removed.

3.5
refractory containing carbon and/or silicon-carbide
formulation containing shaped or unshaped products containing SiC and/or carbon

3.6
nitride and oxynitride bonded silicon carbide refractory
product predominantly consisting of silicon carbide with minor amounts of nitride phases as a matrix component

Note 1 to entry: In general, metallic silicon is used as precursor material for silicon carbide that undergoes a phase transformation in an oxygen-free nitrogen atmosphere.

Note 2 to entry: Whereas carbon can be available as graphite, organic binder (for example: pitch, tar, resin, carbon black), the SiC content in refractory material can vary from less than 1 % by mass to almost 100 % by mass.

3.7
free carbon
carbon species such as graphite, amorphous carbon (carbon black) and organic carbon (pitch, tar or resin)

3.8
free metallic component
metallic species which is added to refractories or appear as residual component in raw materials because of their production process, including treatment

EXAMPLE Si in SiC.

Note 1 to entry: This includes metallic components which are formed in, and remain through, the firing process (for example: free silicon, free aluminium, and free magnesium).

3.9
oxide bond component
metal oxide species which is added as a compound to refractory admixtures or occur as residual component in raw materials due to their production process

EXAMPLE SiO_2 in SiC.

Note 1 to entry: SiO_2 has to be differentiated concerning combined SiO_2, free SiO_2 and surface SiO_2.

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4 Sampling and preparation of the test sample

4.1 General

Sampling shall be carried out in accordance with ISO 5022 for shaped refractory products and ISO 8656-1 for unshaped refractory products unless otherwise agreed by the user and the producer.

NOTE Information on sampling procedures for the analysis of bulk particulate materials is given in ISO 11648-2[18].

4.2 Sample pre-treatment

4.2.1 General

To avoid preparation dependent inaccuracies for the results, the samples shall be prepared as described in 4.2.2 and 4.2.3.

4.2.2 Crushing

With the exception of raw materials, samples are generally in large pieces that require jaw crushing prior to the fine-grinding stage. Due to the risk of contamination, particularly by iron, it is essential that size reduction in jaw crushing is the minimum possible, commensurate with obtaining a representative sample and achieving the maximum size that can be tolerated at the subsequent fine grinding stage.

If free iron or total iron is required, a separate sample should be crushed in an iron-free device.

In the fine grinding stage, it is essential to use the minimum amount of grinding, as excessive grinding will oxidize silicon carbide and silicon nitride to silica.

EXAMPLE Grinding a sample to <75 µm rather than <125 µm could increase the free silica by between 0,06 % and 0,4 % and decrease the SiC by between 0,04 % and 0,25 %.

To produce a test sample with the minimum of oxidation, carefully grind and sieve the material through a 150 µm sieve. Due to the hardness of these materials, it is preferable to fine grind (in such a manner as to reduce the size to <150 µm) using a tungsten carbide vial in a swing mill, or alternative mills lined with tungsten carbide or lined with any material that does not contaminate the sample with any of the analytes to be determined. The grinding process will inevitably generate contamination due to abrasion of the vial material, and, if excessive contamination is to be expected, corrections shall be made to the analysis, in terms of dilution of the sample by the grinding media, to the loss on ignition due to the gain in weight on oxidizing tungsten carbide. These corrections require a factor to allow for the cobalt or nickel binder in the grinding material, in accordance with ISO 12677:2011, Annex B.

Similarly, in the case of free carbon and total carbon determinations, 0,051 8 % of carbon shall be subtracted for each 1 % of tungsten oxide found in the analytical sample, the carbon figure shall then in turn be corrected for the dilution factor above. When tungsten carbide grinding media are not available, prepare two analytical samples, one using an alumina mortar or vial and the other using an iron percussion mortar. Use the sample prepared in the iron mortar for determinations except for total iron and free iron. Use the alumina ground sample for total iron, free iron and free silicon.

4.2.3 Thermal pre-treatment – Drying

For chemical analysis, the sample shall be in a dry state. Dry the sample at 110 °C ± 10 °C to constant mass.

NOTE 1 Drying overnight is usually sufficient.

Chemically bonded water and volatiles in pitch and resin can be already affected by this sample treatment, but they are not removed quantitatively at 110 °C. In this case, special heat pre-treatments are required. For pitch bonded materials a thermal treatment at 200 °C for 18 h and for resin bonded materials 400 °C for 18 h are recommended.

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5 Preliminary analyses

If the principal composition of the testing material is unknown, then preliminary analysis as follows is required.

The presence of other silicon species besides SiC or SiO_2 in the sample (for example, silicon, silicon nitride, sialon, silicon oxy-nitride) shall be checked by carrying out a semi-quantitative analysis by X-ray diffraction (XRD) in accordance with ISO 21068-4.

NOTE 1 The presence of free aluminium can be determined with this method.

NOTE 2 With XRD, the detection limits can vary because of the crystal structure (approximately between 0,1 % and 1 % by mass).

In addition to a preliminary XRD analysis, a qualitative test for nitrogen should be carried out by placing 0,5 g of the powder sample in a dry boiling tube, adding a few pellets of NaOH and heating over a Bunsen burner until the pellets melt. Test for any ammonia evolved with a wet pH indicator paper. If no significant quantity of ammonia is detected, the nitrogen determination may be omitted.

6 Expression of results

Calculate the test results as a percentage composition (mass fraction) and express the result as the mean of two determinations. The results shall be rounded depending on the uncertainty of the measurement.

7 Test report

The test report shall contain as a minimum the following information:

a) all information necessary for identification of the sample tested;

b) a reference to the part of the ISO 21068 series applied for the analyses, including its year of publication;

c) the method used for sampling;

d) the chemical components determined;

e) the specific details of the methods used;

f) the results of the tests, including the results of the individual determinations and their mean, calculated as specified in each part of the ISO 21068 series and expressed in accordance with Clause 6;

g) if available,

   1) bias from sample preparation, and

   2) the precision and bias of measurement;

h) any deviations from the procedure specified;

i) any unusual features (anomalies) observed during the test;

j) the date of the test;

k) the name and address of laboratory and signature of responsible person.

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